Uranium in agricultural soils and drinking water wells on the Swiss Plateau

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Abstract

Mineral phosphorus fertilizers are regularly applied to agricultural sites, but their uranium (U) content is potentially hazardous to humans and the environment. Fertilizer-derived U can accumulate in the soil, but might also leach to ground-, spring and surface waters. We sampled 19 mineral fertilizers from the canton of Bern and soils of three arable and one forest reference sites at each of four locations with elevated U concentrations (7–28 µg L^{-1}) in nearby drinking water wells. The total U concentrations of the fertilizers were measured. The soils were analysed at three depth intervals down to 1 m for general soil parameters, total Cd, P, U and $NaHCO_3$-extractable U concentrations, and $^{234/238}U$ activity ratios (AR). The U concentrations and AR values of the drinking water samples were also measured. A theoretical assessment showed that fertilizer-derived U may cause high U concentrations in leaching waters (up to approx. 25 µg L^{-1}), but normally contributes only a small amount (approx. 0–3 µg L^{-1}). The arable soils investigated showed no significant U accumulation compared to the forest sites. The close positive correlation of AR with $NaHCO_3$-extractable U ($R = 0.7$, $p < 0.001$) indicates that application of fertilizer can increase the extractable U pool. The lack of depth gradients in the soil U concentrations (1.5-2.7 mg kg^{-1}) and AR (0.90-1.06) ratios are inconsistent with the accumulation of U in the surface soil, and might indicate some leaching of fertilizer-derived U. The AR values in the water samples were close to 1, possibly suggesting an influence of fertilizer-derived U. However, based on findings from the literature and considering the heterogeneity of the catchment area, the agricultural practices, and the

comparatively long distance to the groundwater, we conclude that fertilizer-derived U makes only a minor contribution to the elevated U concentrations in the water samples.

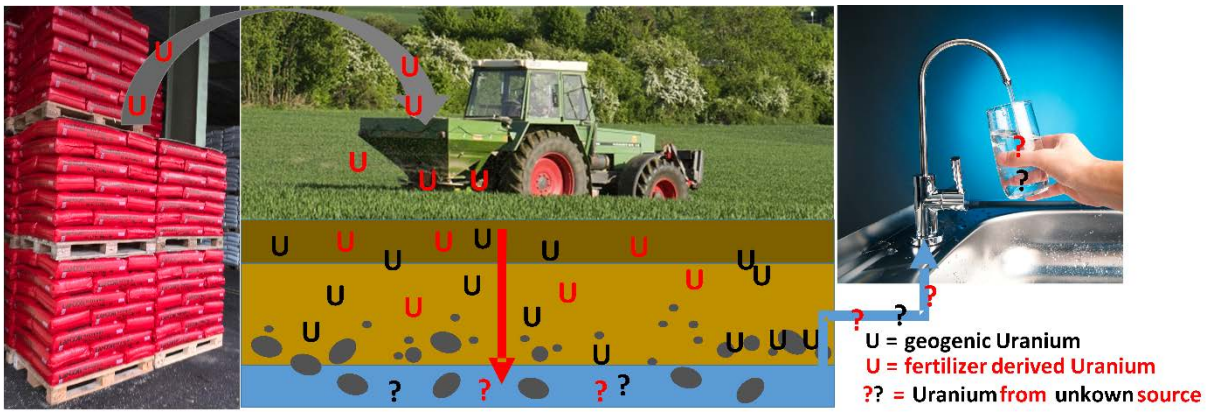
Keywords: Uranium, mineral fertilizer, soil, water, activity ratio

Capsule: Mineral fertilizer application causes an increase of $NaHCO_3$-extractable U in soil, and might significantly contribute to U concentrations in waters at background levels, but is probably only a minor contributor at high U concentrations in the waters of the Swiss Plateau.

Highlights:

- Mineral P fertilizers contain high U concentrations.
- Mineral fertilization could cause high U concentrations in waters.
- The concentration of extractable U is linked to mineral fertilizer application.
- No accumulation in the surface soil might indicate partial leaching of U.
- Fertilizer-derived U is probably only of minor importance for water concentrations.

Graphical Abstract



Introduction

Mineral based phosphorous fertilizers are regularly applied to many agricultural sites, but often contain high concentrations of U. Depending on the soil conditions, fertilizer-derived U might be mobile and contaminate ground- and surface waters (Birke and Rauch, 2008; Huhle et al., 2008; Schnug and Lottermoser, 2013). Finally, the U may end up in drinking water, which is the major source for human uptake of toxic U (65%–95% of total U uptake; Schnug, 2012).

Mineral based phosphorous fertilizers are produced from phosphate rocks of igneous or sedimentary origin. Depending on the source, sedimentary phosphorites are heavily enriched in U (up to 280 mg kg^{-1}; McLaughlin et al., 1996). During the process of fertilizer production, U is enriched in the fertilizers by up to 150% (Sattouf, 2007). Thus, different types of fertilizers (e.g. triple superphosphate and diammoniumphosphate) may have very different U contents (Table S1) depending on the source and type of production. When mineral based fertilizers are applied to soil, they are rapidly solubilized and the mobilized U can be sorbed to soil components, precipitated, or leached. Uranium binds to organic matter, Al and Fe oxides, clay minerals and soil organisms (Echevarria et al., 2001; Zheng et al., 2003; Zielinski et al., 2000). For soils with high clay and organic-matter content, U is anticipated not to migrate substantially (Rogasik et al., 2008). Accordingly, several studies have shown that long-term fertilization with mineral based P-fertilizers leads to substantial accumulation of U in soils, particularly topsoil, compared to unfertilized soils (Bigalke et al., 2017; Jones, 1992; Rogasik et al., 2008; Schipper et al., 2011; Takeda et al., 2005, 2006; Taylor, 2007; Wetterlind et al., 2012; Yamaguchi et al., 2009; Zielinski et al., 2006). In accordance with these findings, a number of authors have pointed to regional variations in concentrations of U in drinking water generally related to bedrock composition, even if the direct relationship might be complicated by groundwater flow through different rock formations (CCME, 2011; Stalder et al., 2012). However, a number of studies also found indications of U transfer from fertilizers to water bodies (Azouazi et al., 2001; Barisic et al., 1992; Conceicao and Bonotto, 2003; Huhle et al., 2008; Smidt et al., 2012; Zielinski et al., 2000). The influence of fertilizer-derived U inputs can be tested by comparing fertilized and unfertilized reference sites (Birke and Rauch, 2008; Huhle et al., 2008; Rogasik

et al., 2008) or from correlations between U and other fertilizer-derived components such as nitrate, K and B, especially in shallow drinking waters at agricultural sites (Knolle, 2008; Popit et al., 2004; Schäf et al., 2007; Smidt et al., 2012).

One important reason for the different findings in terms fertilizer U transfer to groundwaters is the U mobility in soils. The pH is one of the most important drivers of U mobility in soils (Echevarria et al., 2001; Tylor and Olsson, 2001). The lowest mobility of U is around pH 7 but mobility increases with decreasing pH because of decreasing number of binding sites and changes in U speciation. Depending on pH and the presence of organic and inorganic ligands such as phosphates (PO_4^{3-}), carbonates (CO_3^{2-}), sulphates (SO_4^{2-}), chlorides (Cl^-) or fluorides (F^-) U forms stable complexes of different mobilities (Bourdon et al., 2003; Vandenhove et al., 2007). Especially under slightly alkaline and oxic conditions -as they are common in many Swiss agricultural fields- U is therefore quite mobile (Jacques et al., 2006). The presence of carbonates particularly increases the mobility of U in alkaline soils because U–carbonate complexes are predominantly neutral or negatively charged and have a low affinity for soil minerals (Echevarria et al., 2001; Read et al., 2008; Zheng et al., 2003). Besides pH and complexing agents the amount of possible binding sites (organic material, Fe oxides and clay) controls the possible U sorption (Rogasik et al., 2008). Depending on soil properties, U does or does not significantly accumulate in soils but is readily transferred to aquifers (Hamamo et al., 1995; Mortvedt, 1994), especially if the ground water table is close to the soil surface (Huhle et al., 2008) .

The $^{234}U/^{238}U$ alpha activity ratio (AR) is a tool to relate U to its source directly. In an undisturbed closed system, as is assumed in a phosphate rock deposit, a secular equilibrium becomes established and AR levels approach 1 (Figure 1; Bourdon et al., 2003; Keith et al., 2007). Conversely, recoil processes and the spontaneous oxidation of U^{4+} to U^{6+} during decay are reasons for preferential leaching of ^{234}U from soil, leaving it with AR < 1 and the leaching water with AR > 1 (Osmond and Cowart, 1976). The extent of $^{234/238}U$ disequilibrium depends on the characteristics of the disturbance and values of 0.8–10 in waterbodies, 0.8–8 in precipitation and 0.5–1.2 in soil have been reported (Keith et al., 2007). The contribution of fertilizer-derived

U to soils, surface and groundwater can therefore be recognized by a shift in AR towards 1, which has been successfully used in a number of studies to trace the sources of U in soil and water (Conceicao and Bonotto, 2003; Zielinski et al., 1997, 2000, 2006).

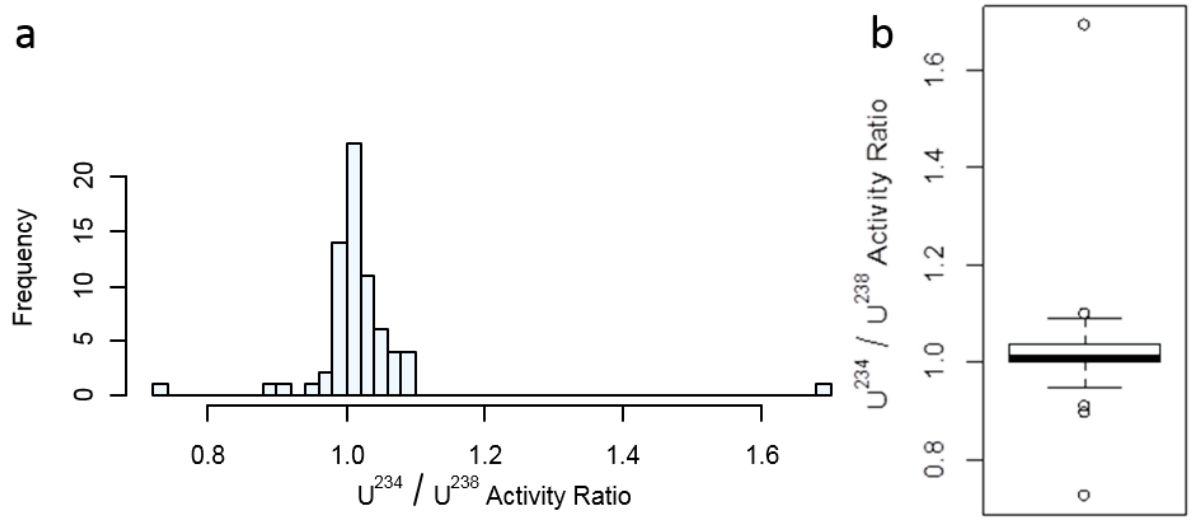


Figure 1 a) Frequency distribution of AR in 65 mineral based P fertilizers; b) Boxplot of AR values of P fertilizers. The bold black line in the box, shows the median, the upper and lower end of the box show the upper and lower quantile. The whisker represent the lowest and highest value, which is still within 1.5 times the interquartile range. Dots above and below the whiskers can be considered as outliers. Data from Baeza et al. (2011), Conceicao and Bonotto (2003), Gafvert et al. (2001), Guimond and Windham (1975), Makweba and Holm (1993), Mangini et al. (1979), Osmond and Cowart (1976), Sattouf (2007), Saueia and Mazzilli (2006), Taylor (2007) and Zielinski et al. (1997, 2000, 2006).

To study the influence of fertilizer-derived U on concentrations in soils and its possible leaching, we sampled soils from four agricultural catchments that showed elevated U concentrations in drinking water wells. These areas are under intensive agricultural usage and there is no obvious source of the high U in the water wells. The aims of this study were to determine:

1. whether fertilizer-derived U has the potential to cause significantly elevated U concentrations in ground- and surface waters,
2. whether there is any indication of fertilizer-derived U enrichment in the agricultural soils and,
3. whether there is any indication of U leaching from the soils.

Material and Methods

Study sites

Four study locations in the canton of Bern, Switzerland were chosen because of the occurrence of elevated U concentrations in ground- and spring waters (Table 1) nevertheless the geology is very similar to other sites with low U in waters. The locations Oberwil bei Büren (pumping station at Rossmatt), Oberwil bei Büren (well at Rüti), Ins (well) and Walliswil (well) were selected. All locations are in the Swiss molasse basin (Figure S1). The agricultural fields and the nearby forest sites have similar underlying geology (www.geo.admin.ch). The two locations in Oberwil bei Büren (Rossmatt and Rüti) are close to each other and the area is underlain by Quaternary unconsolidated rock, mainly till from the last glaciation (Würm). The forest at Rüti covers the same formation, and the forest at Rossmatt lies on the same formation but is close to Tertiary molasse (Lower Freshwater Molasse) of the Zinshölzli Formation under a thin Quaternary cover. The pumping station at Rossmatt pumps water from 40m depth. The water permeability is classified as normal for all fields, and the water-retention capacity is moderate to good. In Ins the agricultural fields and the forest site are situated on grey-green shell sandstones and marl of the Upper Marine Molasses. The springs are located on clayey marls, freshwater limestone and grey sandstones. The water permeability is characterized as normal with a good water-retention capacity. In Walliswil the area contains Quaternary unconsolidated rocks, probably from the last glaciation (Würm). The water permeability for the Walliswil sites is classified as excessive and the water-retention capacity as low. However, the forest site in Walliswil has a loose surface layer, the highest C_{org} concentrations, and a name indicating a historical peat land (Dängelmoos). In addition, local knowledge indicates that the forest site receives significant amounts of drainage water/surface runoff from other agricultural and forested sites. The water chemistry of all waters is dominated by dissolved Ca^{2+} (90-131 mg L^{-1}) and Mg^{2+} (5.9-26.9 mg L^{-1}; total hardness 3.3 - 3.7 mmol L^{-1}), with less Na (3.3-16 and K (0.9-4.6) and has a neutral to slightly alkalic pH. The dominating soils are Cambisols, while at some sites also Luvisols might have formed (FAO, 2006). The depth of the ploughed surface horizon is between 25-30 cm, regular manure application is likely on most of the fields. Irrigation of the field sites is unlikely as mainly crops are grown which are not irrigated in this part of Switzerland (wheat, corn, grass etc.; Fuhrer 2014)

Table 1: Uranium concentrations and AR in drinking water wells

Location	Type of water (Concession volume [l min^{-1}])	Uranium concentration [µg L^{-1}]	$^{234/238}U$ Activity Ratio
Rossmatt	Groundwater (101–250)	27.97	1.22
Rüti	Spring tap 1 & 2 (315 & 370)	12.01	1.22
Walliswil	Groundwater (40)	7.4	-
Ins	Spring tap (40)	20.34	1.11
Ins Schlosshubel	Spring tap 1 (-)	8.13	1.05
	Spring tap 2 (40)	15.82	0.99
	Spring tap 3 (-)	12.39	1.06

Sampling

At each study site three agricultural fields and one forest were sampled. The arable sites were always located in the direct water protection area (inflow area) of the corresponding drinking water well. The information about the inflow areas are taken from the water protection maps (geoadmin.ch), and are mainly based on test with fluorescent tracers in the past (personal communication Bruno Schlup, responsible person for the Rüti Well). One nearby forest site was chosen at every location as an unfertilized reference site. At each of the sites soil was sampled with a soil auger down to 1 m depth in ten replicates evenly distributed over the sites. The samples from all sites were separated into subsamples from depths 0–30, 30–60 and 60–100 cm. In addition, for field C at Ins the last depth interval was subdivided because of obvious changes in colour and structure. One composited sample was prepared from the 10 replicates for each depth. In total twelve arable sites and four forest sites were sampled at three depth intervals. For analytical purposes nineteen commercially available fertilizers were bought from shops in the canton of Bern. In total six PK (phosphorous potassium), six superphosphates, six NP (nitrogen phosphorous) and one MKP (monopotassium phosphate) fertilizer were sampled. Water samples were collected from the pumping station and the water wells in plastic bottels, filtered (0.45µm) and acidified (HNO_3) directly after sampling.

178 **Soil characterization**

179 After sampling the 49 soils were dried at 40°C, aggregates were crushed and the sample was
180 sieved to ≤2 mm using a stainless steel sieve. The pH was measured in 0.01-M $CaCl_2$ with a
181 soil solution ratio of 1:2.5 after 2 h using a glass pH electrode. To determine the effective cation
182 exchange capacity (ECEC) and base saturation, 5 g of soil was extracted in 100 ml of 1 M
183 ammonium nitrate (NH_4NO_3) solution on a horizontal shaker for 1 h. The concentrations of
184 calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), manganese (Mn) and aluminium
185 (Al) were measured with flame atom absorption spectrometry (ZEEnit 700P, Analytik Jena).
186 ECEC was then calculated as the sum of the charge of the exchangeable Ca^{2+}, Mg^{2+}, K^+, Na^+,
187 Al^{3+} and Mn^{2+} ions, and is expressed in $mmol_c\ kg^{-1}$. Base saturation was calculated as the
188 percentage of the charge of basic cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) of the ECEC.
189 For texture analysis an aliquot of the soil was oxidized by heating with H_2O_2 to remove all
190 organic material. Samples were then washed and finally dispersed in a sodium
191 hexametaphosphate/sodium carbonate solution. Particle-size distribution was measured using
192 a laser diffraction particle-size analyser (Mastersizer 2000, Malvern, Herrenberg, Germany).
193 The average relative standard deviation of repeated samples was 8%. For total element
194 concentrations and analysis of carbon, nitrogen and sulphur (CNS), an aliquot of each soil
195 sample was ground in a ball mill in agate beakers (PM 200, Retsch GmbH, Haan, Germany).
196 Rock samples were crushed using a jaw breaker and ground with the same ball mill. The CNS
197 concentrations were analysed by elemental analysis (vario EL cube, Elementar
198 analysesysteme, Hanau, Germany) on both 550°C-heated (only inorganic C) and untreated
199 (organic and inorganic C) samples: the amount of organic C (C_{org}) was calculated from the
200 difference between the two values.
201

202 **U analysis**

203 The extractable U fraction was extracted in 0.5 mol $NaHCO_3$ (pH 8.5) after 16 h of shaking at
204 a soil/solution ratio of 1:60. After shaking the sample was filtered (Whatman, Grade 589/2) and
205 the supernatant was analysed for U concentrations. Total digestions were performed in a

206 microwave oven with 0.1 g of pulverized sample, 0.5 ml H_2O_2 (30%), 2 ml HF (40%) and 2 ml
207 HNO_3 (69%) at 200°C for 40 minutes. A second run was carried out after adding 10 ml of 6%
208 boric acid (H_3BO_3), at 180°C for 30 minutes to complex the remaining HF. Total digestions of
209 fertilizers were undertaken in 8 ml HNO_3 (69%) and 2 ml H_2O_2 (30%) in a microwave oven at
210 200°C. Total element concentrations were measured using an inductively coupled plasma
211 mass spectrometer (ICP-MS; 7700x, Agilent Technologies, Palo Alto, CA) with ^{103}Rh and ^{115}In
212 as internal standards. The applied method was tested using standard reference material
213 (BCR-2, United States Geological Survey, Reston, Virginia) and showed good agreement
214 between measured (1.73±0.08 mg kg^{-1}, n = 4) and certified (1.69±0.19 mg kg^{-1}) values.
215 For the AR analysis, 0.1 g of the pulverized samples were weighed in Savillex beakers and
216 heated on a hotplate in 2.4 ml HF (40%) and 0.8 ml HNO3 (69%, 3:1 ratio) for 48 h. The digest
217 was dried down and the remaining residues treated with 750 µl HCl and 250 µl HNO3 (3:1
218 ratio) and evaporated. The samples were redissolved in 4 ml of 3 M HNO_3 and purified
219 following the method of Weyer et al. (2008) on UTEVA (Eichrom Technologies Inc.) U specific
220 resin. We modified the method using 9 M HCl to convert the columns from the nitric to the
221 chloric system as proposed by the manufacturer of the columns (Eichrom Technologies Inc.,
222 2005). The purification procedure showed good separation of U (Figure S2). In total, 99% of
223 the total eluted U was collected in the U fraction and the concentrations of Th and Fe were
224 less than 0.1% of that of U. Recovery rates for the BCR-2 reference material after column
225 purification were 90%±9% (n = 3), comparable to the results of Grinberg et al. (2005). The
226 recoveries were considered sufficient because the isotope ratio is not affected by the
227 separation process (Weyer et al., 2008). The total blank of the method was <0.4% of the lowest
228 concentrations in a sample.
229 Isotope ratios were analysed on the same Quadrupole ICP-MS as was used for the element
230 concentrations. Before analysis, all standards and samples were diluted to a concentration of
231 12.5 µg L^{-1} and the instrument settings were adjusted to allow highly accurate U isotope
232 analysis (five replicates, 1000 sweeps/replicate, integration time 0.3, 0.3, 0.99, 50.01, 5.01
233 and 0.99 seconds for mass 103, 115, 232, 234, 235 and 238, respectively). ^{103}Rh and ^{115}In

were used as internal standards and ^{232}Th was monitored to detect possible interference. The isotope ratio was mass bias corrected using the standard bracketing method (Albarède and Beard, 2004). IRMM 3184 (Institute for Reference Materials and Measurements, Geel, Belgium) was used as the bracketing standard. The measured isotope ratios were transformed to activity ratios using the specific activity of each isotope. We repeatedly analysed BCR-2 for quality control. The results (1.000±0.004, mean ± SD, n = 12) agree well with the values of 1.000±0.001 reported by Beier et al. (2010a, b) and of 1.001±0.002 reported by Keech et al. (2013). The overall reproducibility was similar for the BCR (±0.004, SD, n = 12), an in house standard (±0.004, SD, n = 6) and repeated sample digests (±0.007, SD, n = 6) and sufficient at the overall variation of AR in the samples (0.906-1.065).

Assessment of possible U leaching

Using available information about fertilizer use in Switzerland (Agristat, 2013; BLW, 2014; GRUDAF, 2009) and the U concentrations in the fertilizers, estimates of U leaching were obtained on an annual basis. The estimate of the possible contribution of fertilizer-derived U to the U concentration in water was based on certain assumptions. Two scenarios were tested. The first scenario, the “average scenario”, was based on average values for fertilizer application (GRUDAF, 2009), U content in the fertilizer (Figure 2), leaching rate and infiltration rate (von Gunten, 2000). A second estimate was calculated using a “high scenario” with a high fertilizer application rate (for fodder beet, the culture with the highest P demand according to GRUDAF [2009]). A correction factor of 1.25 was applied, what means that 25% more fertilizer can be applied to compensate for lower than normal P concentrations in the soil. For the high scenario, a fertilizer with high U concentration (90^{th} percentile, Figure 2), the maximum leaching rate and a high infiltration rate was assumed (von Gunten, 2000). The maximum correction factor for P fertilization according to GRUDAF (2009) was not applied because it seems unlikely that a P-demanding crop is cultivated on a field where such a correction factor would apply. The infiltration on the Swiss Plateau is 250–700 mm a^{-1} (Von Gunten, 2000).

Statistical Analysis and geochemical mass balancing

Differences between groups (e.g., between forest and arable soils) were tested using a two sided t test.

Geochemical mass balances of U were calculated as τ-values following Brimhall et al. (1992) using Ti as an immobile element. The τ-value is a measure for the depletion (negative value) or enrichment (positive value) of an element in a soil relative to the bedrock and corrected with an immobile element. A τ-value of 0.5 for example would indicate an enrichment of U by 50% compared to the bedrock.

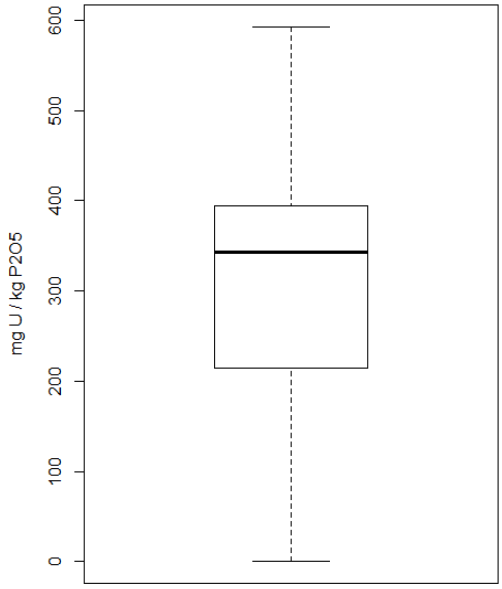


Figure 2: Boxplot of U concentrations in 19 mineral based P-fertilizers sampled in the canton of Bern. The bold black line in the box, shows the median and the upper and lower end of the box show the upper and lower quantile. The whisker represent the lowest and highest value, which is still within 1.5 times the interquartile range.

Results

The mean U concentration in the analysed fertilizers was 294 mg kg^{-1} P_2O_5; the median value was 343 mg kg^{-1} P_2O_5 (Figure 2, Table S1). The lowest and highest U concentrations were 0.21 and 593 mg kg^{-1} P_2O_5. The mean and median U concentrations compared to the dry weight of fertilizer were 77.8 and 69.6 mg kg^{-1}, with a range of 0.11–188 mg kg^{-1}. Comparably

high concentrations were detected for PK (mean 386 mg kg^{-1} P_2O_5; n = 4), superphosphate (mean 358 mg kg^{-1} P_2O_5; n = 4) and NP-fertilizers (mean 348 mg kg^{-1} P_2O_5; n = 4), whereas DAP U concentrations were one order of magnitude lower (mean 25.1 mg kg^{-1} P_2O_5; n = 3). The assessment of the possible contributions of fertilizer-derived U to the U concentrations of leaching water indicated significant contributions (Table 2), compared to concentrations in Swiss drinking waters (median 0.77 µg L^{-1}; Stalder et al., 2012). However, even in the rather unlikely high scenario, fertilizer-derived U does not cause exceedance of the World Health Organisation (WHO) threshold level for drinking water (30 µg L^{-1}).

Table 2: Estimation of the possible contribution of mineral based P fertilizers to U in ground- and well water.

	"Average" scenario	**"High" scenario**
Mineral based fertilizer application rate	36.8 kg P_2O_5 ha^{-1}	150 kg P_2O_5 ha^{-1}
U concentration in fertilizer	294 mg kg^{-1} P_2O_5	509 mg kg^{-1} P_2O_5
U input via fertilization	10.8 g ha^{-1}	76.4 g ha^{-1}
Infiltration rate	600 mm a^{-1}	300 mm a^{-1}
Leaching amount	50%	100%
U concentration in leaching water	**1.80 µg L^{-1}**	**25.5 µg L^{-1}**

The forest soils showed generally lower pH and ECEC values than the arable soils. Only the Walliswil arable sites exhibited lower pH and ECEC values than the forest site (Table 3). The deviation in soil properties and AR in the Walliswil forest site can be explained by the fact that the soil was located at slightly lower elevation than the arable area and probably received leaching water that was enriched in nutrients, carbonate and U with AR > 1. High soil moisture caused a relative accumulation of organic carbon (Table 3), which could lead to U sorption to organic compounds or precipitation under anaerobic conditions in the peat (Regenspurg et al., 2010). This was also confirmed by the visual impression of the site at the

time of sampling. The topsoil had quite a large organic overlay, probably caused by reduced decomposition under wet conditions. The name of the site (Dänglermoos) and personal communication with farmers indicate that the area is a former peatland. A cluster analysis based on the soil properties of all soils confirmed that the Walliswil forest site is different from all other soils. Because of these extraordinary features, the forest site at Walliswil was excluded from further comparison and is not included in Figures 3–4.

In contrast, C_{org} was always higher in the forest topsoils. Except for these differences, forest soils did not differ from agricultural soils. The difference in the mean U concentration between fields and forests of 0.15 mg kg^{-1} (Figure S3, S4) was statistically not significant ($p = 0.21$), which might, however, also be attributable to the small number of samples (especially for the forest sites) and the variation between the individual sites. The U_{NaHCO3} concentrations also exhibited a tendency to be higher at arable sites compared to forest soils, but this difference was not significant at all depths (Table 3). The τ_U values tend to be lower in forests compared to agricultural fields at each individual site except Walliswil, although these differences are only marginally statistically significant ($p = 0.07$). The difference was about 0.2 over the whole depth of the profile, indicating about 20% more loss of U at the forest sites (Figure 3a). In addition, Cd, which has a high concentration in mineral based P-fertilizers (McLaughlin et al., 1996), exhibited no significant enrichment in the arable sites compared to the forest ones ($p = 0.77$; Figure 3b), whereas this difference was highly significant for P down to 60 cm depth (0–30 cm, $p = 0.001$; 30–60 cm, $p < 0.001$; Figure 3c).

The AR values were generally not different or higher in agricultural topsoils compared to subsoils (Figure S5, S6, Table 3). Compared to forest soils, the AR values at the agricultural sites were only consistently higher in Rossmatt, but were overlapping in Ins and Rüti and clearly lower in Walliswil. Overall, there is a highly significant correlation ($p < 0.001$) between the amount of extractable U and AR (Figure 4). However, for individual sites the correlation is significant for Rossmatt ($p < 0.001$), Walliswil ($p < 0.001$), and marginally significant for Ins ($p = 0.08$) but not significant for Rüti ($p = 0.62$; Figure S4). The AR values in the well water were between 0.99 and 1.22 (Table 1).

335 *Table 3 Soil properties, concentrations of selected elements and $^{234/238}U$ activity ratios of all soils.*

Site	Field	Depth	pH	CEC	Base sat.	Clay	Silt	Sand	C_{org}	P	Cd	Th	U_{total}	U_{NaHCO3}	$^{234/238}U$	SD
		[cm]		[mmol kg^{-1}]			[%]					[mg kg^{-1}]			Activity Ratio	
Oberwil Rossmatt	Forest	0 - 30	3.9	34	42	10	35	56	1.70	389	0.14	6.85	2.02	0.13	0.940	0.005
		30 - 60	4.0	27	30	7	25	68	0.62	248	0.09	6.30	1.54	0.14	0.937	0.002
		60 - 100	6.4	151	100	9	31	60	0.26	304	0.11	7.66	1.68	0.05	0.930	0.004
	Field A	0 - 30	5.1	67	99	8	39	53	1.31	741	0.23	5.96	2.29	0.24	1.001	0.004
		30 - 60	5.4	74	99	7	37	56	0.83	511	0.17	6.29	2.17	0.25	0.994	0.006
		60 - 100	6.8	-	100	9	43	48	0.51	294	0.13	5.64	1.89	0.22	0.999	0.001
	Field B	0 - 30	5.5	64	99	8	35	57	1.24	708	0.20	6.08	1.99	0.30	1.007	0.023
		30 - 60	5.5	63	99	7	34	58	0.63	584	0.17	6.77	1.93	0.17	0.964	0.001
		60 - 100	5.5	68	100	6	30	64	0.34	582	0.17	6.75	1.86	0.14	0.967	0.001
	Field C	0 - 30	5.6	101	100	10	43	47	1.67	612	0.18	5.62	1.64	0.57	1.054	0.005
		30 - 60	5.8	81	100	9	37	55	0.96	532	0.17	6.21	2.06	0.32	1.046	0.006
		60 - 100	5.8	68	100	8	34	58	0.45	438	0.14	6.82	1.94	0.49	1.036	0.004
	Rock	-	-	-	-	-	-	-	-	707	0.11	3.79	1.21	-	0.922	0.005
Walliswil	Forest	0 - 30	6.2	-	100	7	38	55	4.36	903	0.40	5.81	2.03	0.37	1.006	0.004
		30 - 60	6.4	-	100	9	41	50	2.49	890	0.25	6.86	2.50	0.55	1.036	0.006
		60 - 100	6.4	-	100	9	45	46	1.52	806	0.26	7.02	2.52	0.69	1.065	0.007
	Field A	0 - 30	5.4	64	99	8	55	37	1.31	871	0.20	7.10	2.23	0.24	0.975	0.004
		30 - 60	5.1	52	100	9	58	33	0.75	758	0.18	8.50	2.21	0.18	0.956	0.001
		60 - 100	5.0	64	100	6	44	50	0.35	476	0.12	8.73	2.17	0.15	0.939	0.000
	Field B	0 - 30	5.2	75	99	10	40	51	2.53	1222	0.22	6.73	1.95	0.20	0.966	0.002
		30 - 60	5.1	51	100	8	34	58	1.37	814	0.17	6.77	1.76	0.18	0.959	0.005
		60 - 100	5.3	43	99	12	37	52	0.63	565	0.13	7.32	2.09	0.15	0.906	0.002
	Field C	0 - 30	5.5	72	100	10	41	49	1.81	1386	0.27	5.94	1.96	0.31	0.968	0.000
		30 - 60	5.0	37	99	9	34	57	1.04	792	0.20	6.16	1.85	0.21	0.962	0.005
		60 - 100	5.1	38	99	7	33	60	0.46	453	0.43	7.47	1.95	0.15	0.945	0.003
	Rock	-	-	-	-	-	-	-	-	699	0.21	4.03	0.97	-	0.985	0.005
Oberwil Rüti	Forest	0 - 30	4.3	41	83	7	40	53	1.50	303	0.14	6.37	1.82	0.19	0.980	0.003
		30 - 60	4.4	59	89	7	49	43	0.48	256	0.33	8.68	2.20	0.19	0.972	0.004
		60 - 100	4.8	86	93	6	51	43	0.16	423	0.19	9.57	2.38	0.11	0.980	0.002
	Field A	0 - 30	5.1	63	95	6	40	54	1.02	685	0.42	6.40	2.11	0.24	0.971	0.012
		30 - 60	5.4	82	93	7	43	51	0.32	395	0.16	8.18	2.40	0.17	0.973	0.005
		60 - 100	5.6	93	100	7	52	41	0.12	466	0.17	9.03	2.43	0.14	0.963	0.004
	Field B	0 - 30	6.0	91	100	8	52	40	1.27	737	0.39	7.43	2.33	0.20	0.949	0.003
		30 - 60	5.7	87	100	5	37	58	0.67	521	0.16	8.75	2.20	0.13	0.954	0.001
		60 - 100	6.9	89	100	8	55	37	0.23	607	0.17	5.19	1.97	0.11	0.903	0.002
	Field C	0 - 30	5.8	95	100	9	49	42	1.03	782	0.18	7.12	2.24	0.21	0.964	0.002
		30 - 60	5.9	94	100	8	45	47	0.33	713	0.18	7.65	2.21	0.18	0.959	0.005
		60 - 100	5.7	89	100	7	47	46	0.18	551	0.19	8.49	2.42	0.13	0.933	0.001
	Rock	-	-	-	-	-	-	-	-	531	0.12	5.82	2.25	-	0.969	0.003
Ins	Forest	0 - 30	3.9	59	47	10	47	44	1.69	341	0.31	5.24	1.89	0.23	0.986	0.006
		30 - 60	4.1	42	92	8	42	49	0.56	227	0.08	7.03	2.34	0.25	0.979	0.004
		60 - 100	4.6	92	99	10	45	44	0.26	482	0.10	9.42	2.64	0.23	0.967	0.006
	Field A	0 - 30	4.5	68	99	6	33	60	1.22	501	0.10	6.01	1.58	0.21	0.979	0.013
		30 - 60	5.1	76	99	6	34	60	0.81	540	0.08	7.66	1.79	0.16	0.965	0.004
		60 - 100	5.2	89	100	5	29	66	0.65	501	0.07	8.37	1.95	0.13	0.971	0.008
	Field B	0 - 30	5.7	91	100	8	39	53	0.95	641	0.15	5.85	2.19	0.37	0.976	0.021
		30 - 60	5.7	97	100	9	38	53	0.55	438	0.12	6.64	2.47	0.51	0.989	0.006
		60 - 100	5.9	-	100	9	41	50	0.29	362	0.10	7.52	2.69	0.40	0.987	0.006
	Field C	0 - 30	6.0	73	100	8	41	51	0.95	506	0.80	6.00	2.14	0.25	0.998	0.004
		30 - 60	5.9	66	100	10	42	48	0.63	371	0.10	6.05	1.96	0.22	0.993	0.001
		60 - 90	5.8	82	100	7	40	53	0.27	286	0.08	7.15	2.32	0.17	1.006	0.010
		90 - 100	5.9	95	100	9	48	43	0.18	258	0.08	7.69	2.31	0.17	1.000	0.003
	Rock	-	-	-	-	-	-	-	-	372	0.04	7.12	1.98	-	0.954	0.001

336

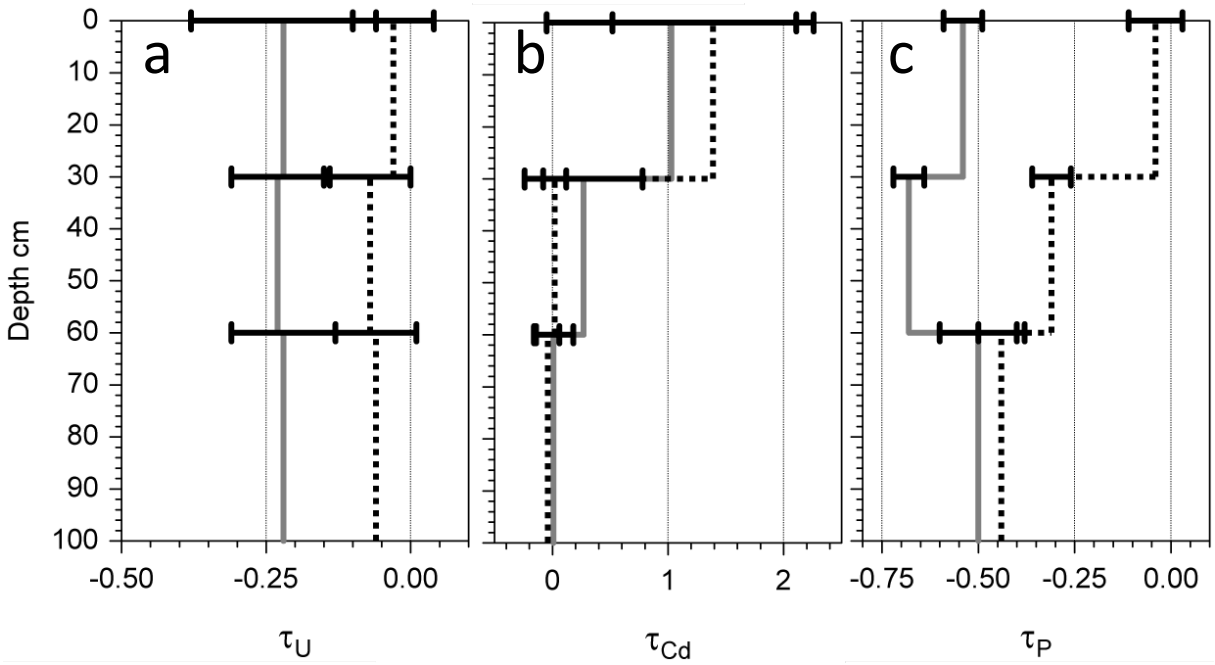


Figure 3 The a) τ_U, b) τ_{Cd} and c) τ_P values of the field and forest soils. Solid grey lines denote forest sites; dotted black lines represent arable fields.

Discussion

General assessment of the possible impact of fertilizer-derived U on drinking water.

The possible effect of fertilizer-derived U on soils and leaching water has been assessed based on the U concentrations in the investigated mineral based fertilizers (Figure 2), official fertilization recommendations for different crop types, infiltration rates from the literature, and assumed leaching rates, for both an average and a high scenario (Table 2).

The assumed U input via fertilization for the average scenario falls well within the range of literature values: 0.13–61 g ha^{-1} (Kratz et al., 2008) and 2.8–16 g ha^{-1} a^{-1} (Uterman and Fuchs, 2008) in Germany; 15 and 16 g ha^{-1} a^{-1} at two sites in England and New Zealand (Rothbaum et al., 1979). The values in the high scenario seem reasonable, as U application in Switzerland has been reported to reach up to 110 g ha^{-1} a^{-1} for certain sites with high-P-demand crops and purely mineral based fertilization in certain years (Bigalke et al., 2017). The most critical aspect of the assessment of U concentrations in leaching water is surely the amount of U leached. In this study, 50% or even 100% is probably an overestimation for most sites; however, the 100% approach is taken to estimate the maximal possible fertilizer-derived U concentration in leaching water.

Uranium output by plant uptake and crop harvesting was estimated to be less than 1 g ha^{-1} (Kratz et al., 2008), leaving 9.8–75 g ha^{-1} a^{-1} in either the soil or leachates (Table 2). Translating this into an increase in U concentration in the topsoils (30cm depth, density 1 kg cm^{-3}) yields a value of 3.3–25 µg kg^{-1} a^{-1}, in good agreement with the compiled annual U accumulation rates in topsoil (0-20 or 0-30 cm depth) of 1–46 µg kg^{-1} from long-term fertilization experiments (Rogasik et al., 2008, Taylor and Kim, 2008). This similarity of U inputs and enrichment in soil indicates that a considerable amount of the applied U is retained in the soil. However, Barisic et al. (1992) estimated that 20% of applied fertilizers are transported to drainage channels, whereas Conceicao and Bonotto (2003) assumed that 30%–43% of U in river water is derived from fertilizer application. Furthermore, Rogasik et al. (2008) detected strong differences in the accumulation rates related to different soil properties; conversely, certain soils did not immobilize U to the same extent as others. Therefore, estimation of leached U is quite difficult because of the high uncertainty and lack of measured values. The estimations (Table 2) illustrate that under extreme circumstances (e.g., shallow groundwater, sandy soil, high-P-demand crop, high U concentration in fertilizer) fertilizer-derived U might cause the U concentration in groundwater to be close to the WHO threshold value and to exceed the threshold for drinking water of some countries (e.g., Germany, 10 µg L^{-1}). However, while we assume these extreme cases to be rare, under normal circumstances fertilizer-derived U will not reach values close to the Swiss threshold values but might however significantly contribute to U concentrations in normal Swiss groundwater (median values in Switzerland are 0.77 µg U L^{-1}; Stalder et al., 2012).

Our results fit published results from the literature as an increase in U concentrations in ground water derived from fertilizers has also been shown also in a number of other studies (Azouazi et al., 2001; Barisic et al., 1992; Birke and Rauch, 2008; Conceicao and Bonotto, 2003; Huhle et al., 2008; Zielinski et al., 2000). As an example, near-surface groundwater is 3–17-fold enriched in U in agricultural areas (Huhle et al., 2008) and U concentrations in water in the former West Germany are reported to be higher than in water in the former East Germany (0.741 and 0.462 µg L^{-1}, respectively). The latter has been explained by the lower intensity of

P-fertilization and lower U concentration (P from igneous rocks; Birke and Rauch, 2008; Schulz et al., 2003). In a broad study of U concentrations in drinking water in Switzerland it was determined that elevated concentrations (up to 100 µg L^{-1}) were only attributable to geological factors (Stalder et al., 2012). However, for that study important cantons (e.g., Bern, where our study sites are located) on the Swiss Plateau were not included and fertilizer-derived U was not considered as a source of U. Other studies investigated high U concentrations in surface waters and found geological factors to be responsible for the elevated concentrations (Banning et al., 2013; Schott and Wiegand, 2003; Zielinski et al., 1995, 1997).

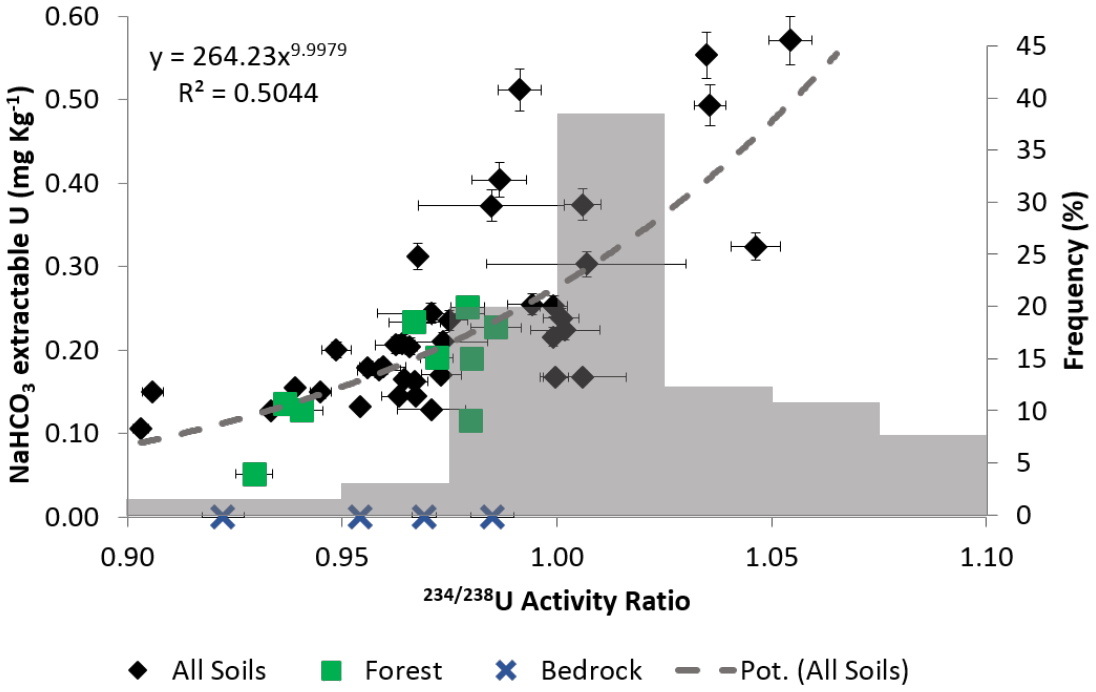


Figure 4: Exponential relationship between AR and $NaHCO_3$-extractable U fraction. The grey bars are the frequency (%) histogram of fertilizer AR values (Figure 1).

Enrichment and sources of U in agricultural soils

Although in our study area U was not significantly enriched at the arable sites (Figures S3), comparable studies reported significant enrichments of 0.1–1.3 mg U kg^{-1} in fertilized soils (Ahmed et al., 2014; Bigalke et al., 2017; Huhle et al., 2008; Rogasik et al., 2008; Rothbaum et al., 1979; Taylor, 2007). The reasons for the broad range might be different sampling depths, different fertilization rates (up to 500–600 kg triple superphosphate ha^{-1} a^{-1}; Taylor, 2007),

403 different U concentrations in the fertilizers and different soil properties (pH, organic matter,
404 redox conditions; Rogasik et al., 2008; Rothbaum et al., 1979). However, many of the soils in
405 the studies received mineral based P-fertilizers annually, whereas in the studied soils, manure
406 application might account for a significant part of the fertilization. Insignificant U accumulation
407 in the surface soil at the studied sites might be partly attributable to surface erosion or leaching
408 of U from the soil.
409 In Rossmatt, Rüti and Ins the AR values of the forest soils are close to those of the local
410 bedrock, but some arable soils exhibit significant deviations (Figures S5, S6, Table 3).
411 Although soil formation should normally lead to AR values smaller than that of the bedrock,
412 this is only the case for Walliswil (except Walliswil forest soils) and Rüti. In contrast Rossmatt
413 and Ins show higher AR compared to the bedrock, indicating higher proportions of fertilizer-
414 derived U, which overcompensate for the weathering effect on the AR (Figures S5, S6).
415 The overall correlation between extractable U and AR indicates a link between high fertilizer
416 U input and the amount of weakly bound U in the soil. As the $NaHCO_3$-extractable U has a
417 higher mobility compared to the rest of the total U, this correlation indicates a contribution of
418 fertilizer derived U to U leaching. The lack of correlation for the Rüti and Ins site might be
419 caused by the topography of the sites. The sites are located on top- and midslope positionsand
420 erosion might eliminate clear patterns because of constant loss of surface soil. On the other
421 hand lateral water flow down the slope might affect AR, because of leaching water with AR>1,
422 which might be sorbed and increase AR of the soil at positions down the slope.
423
424 **Leaching of U in fertilized soils**
425 The distributions of U concentrations, τ_U values and AR values do not exhibit obvious depth
426 gradients (Figures 3, 4, S3-S6). In contrast, the depth gradient is very significant for P, the
427 main component of the mineral based P-fertilizers (Figure 3, Table S1). These differences
428 might be attributable to the much higher P contents compared to the U contents of the
429 fertilizers and the different background concentrations in the soil and to manure fertilization,
430 with low U contents. Assessment of the possible U input in the topsoil (0-30 cm) from the P

enrichment in the topsoil, based on the mean U concentrations of the fertilizers (Figure 2) suggests the U enrichment in the topsoil compared to the subsoil would be around 0.25 mg kg^{-1}. This is close to our (non-significant) mean difference of 0.15 mg kg^{-1} between forest and agricultural sites and to U enrichments reported in Swiss agricultural topsoil compared to subsoils (mean 0.19 mg kg^{-1}; Bigalke et al., 2017). However, while it is well known that high amounts of P are extracted from the soil by plant growth and exported from the soil via harvest, this is not the case for U. Conversely, manure can provide significant inputs of P without adding large amounts of U to the soil. The mean AR ratios show a tendency to be higher in the arable soils, but clearly overlap with the AR values of forest soils and bedrock. Overall, the lack of a U depth gradient indicates a lack of accumulation in the topsoil and thus might suggest U leaching or erosion. However, U might also be sorbed in deeper soil and rock layers, depending on the solution chemistry and speciation of U, and will not necessarily end up in ground- and spring water. In the literature, fertilizer-derived U concentrations in ground- and surface waters were mostly estimated to be <0.5 µg L^{-1} (Birke and Rauch, 2008; Conceicao and Bonotto, 2003; Zielinski et al., 2006) but may reach up to 3.4 µg L^{-1} in drainage water and near-surface groundwater directly in arable fields (Huhle et al., 2008; Zielinski et al., 2000). However, at out study sites the ground- and spring water reservoirs are comparatively deep (many sorption sites), some fertilization was in the form of manure, and not all of the catchment was covered by arable sites. Thus, we assume that contribution to groundwater would rather be lower than the average scenario we calculated (Table 2). From these assumptions, we roughly estimate that leaching of fertilizer-derived U to ground- and spring water is probably less than approx. 2 µg L^{-1}. Comparing this value to the elevated U concentrations in the wells, it becomes clear that there must be additional sources for the elevated U concentrations.

The AR values in natural, unpolluted water samples are 1–4, while a value close to 1 might indicate fertilizer-derived U in the water (Zielinski et al., 1997, 2000, 2006). Thus, the AR values in the waters at our study sites (Table 1) might indicate fertilizer-derived U input, but also a geological basis cannot be excluded.

Conclusions

- Fertilizer-derived U can theoretically cause high U concentrations in waters under extreme conditions, but normally the contribution is rather low (approx. <2 µg L^{-1}). Higher concentrations in waters are normally associated with geogenic inputs.
- The investigated arable sites showed no significant U accumulation compared to the forest sites. The close correlation of bulk soil AR with $NaHCO_3$-extractable U indicate that mineral based P-fertilizer application increases the extractable U pool, which might cause higher leachability.
- The lack of depth gradients of U concentrations, τ_U and AR ratios are not consistent with accumulation of U in the surface soil, which might indicate leaching of fertilizer-derived U. However, based on the calculated U leaching and considering the heterogeneity of the catchment, agricultural practices, and the comparatively long distance to the groundwater, we assume only small contributions (few µg L^{-1}) of the fertilizer-derived U to the elevated U concentrations in the water samples.

Based on the estimated contributions of fertilizer-derived U to U in leaching waters, the correlations of $NaHCO_3$-extractable U and AR, the absence of depth gradients and the AR in the water samples, it is considered likely that U is leached in the soil. However, while the leaching is in a concentration range that might be relevant at normal U concentrations in drinking water, it is only of minor importance at the high concentrations present in the investigated drinking water wells.

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Appendix A. Supplementary data

Supplementary data related to this article can be found online.

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